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Combining Equilibrium Sampling with Non-Target Analysis of Hydrophobic Complex Mixtures in a Complex Matrix

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Risk assessment of complex mixtures is a serious challenge. It is most often based on one-target chemical analysis and one-compound toxicity tests of priority pollutants. However, this approach is meaningless if key contaminants are not known beforehand or the measured compounds do not exert the observed toxicity. Additionally, such chemical analysis is typically based on exhaustive extractions yielding total pollutant concentrations that do not reflect the actual contaminant exposure of organisms. In this study we combine two novel strategies to 1) enrich hydrophobic compounds so that the obtained extracts reflect the available exposure in the matrix and 2) obtain non-targeted chemical fingerprints of these extracts. Sewage sludge is the studied matrix. In 1) equilibrium sampling is performed with jars coated on the inside with micrometer thin silicone PDMS. This polymer is chosen as it provides enrichment for hydrophobic compounds with biological relevant hydrophobicity. When equilibrium partitioning between sludge and PDMS is reached, hydrophobic compounds in the PDMS are back-extracted. This technique provides some unique features for the subsequent instrumental analysis: the compounds are enriched by orders of magnitude in the polymer; typical interferences such as humic acids are excluded, and clean up steps largely omitted. In 2) non-targeted fingerprint analysis of the chemical activity in these extracts are then performed using comprehensive multidimensional gas-chromatography quadruple-time-of-flight with electron and negative chemical ionization (GC × GC-QTOF-EI/NCI), providing high peak capacity and excellent separation. This novel instrumentation also provides the possibility of identification of compound groups in the sewage sludge. Data processing is performed using peak deconvolution algorithms together with pixel-based analysis. The processed data is analyzed with principal component analysis (PCA) to characterize the chemical composition of the sludge samples and determine the main relative differences in the hydrophobic chemical fingerprints. The results presented are supported by total extractions and provide new insight of chemical activity and composition of complex mixtures in complex matrices – the first step towards better risk assessments.